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# Temporal variability in the composition and abundance of terrestrially-derived dissolved organic matter in the lower Mississippi and Pearl Rivers

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**Abstract**

Here we report on temporal changes in the concentration and composition of lignin phenols in high molecular weight (<0.2 μm, >1 kDa) dissolved organic matter (HMW DOM) collected from the lower Mississippi and Pearl Rivers (MR and PR) (USA). Monthly water samples were collected at a station in the lower reach in each river from August 2001 to August 2003. Significantly higher concentrations of lignin and $\Lambda_8$ values (mg lignin phenols in 100 mg organic carbon) in the Pearl River than in the Mississippi River, reflected sporadic inputs of terrestrial DOM during rainstorm events from wetlands and forest soils. Larger seasonal variations in lignin concentration and composition in the Pearl River, compared to the Mississippi River, were attributed to shifts in organic matter sources from topsoil inputs during rainstorm events to groundwater inputs and *in situ* production during base flow in this small river. Conversely, lower $\Lambda_8$ and vanillic acid to vanillin ratios [(Ad/Al)v] in the HMW DOM of the lower Mississippi River may be a result of a lower export rate of lignin from agricultural soils due to lower carbon storage in the expansive agricultural systems of the Mississippi River watershed, as well as dilution of phytoplankton DOM inputs. Large seasonal changes in lignin concentration and $\Lambda_8$ (linked at times with river discharge), and minimal variability in the composition of lignin phenols, likely represented an integrated signal of soil-derived vascular inputs from the upstream drainage basin. If we are to better understand the controls of organic matter delivery to the coastal zone from both small and large rivers, sampling strategies need to be adjusted to account for the different scales of hydrologic response time and *in situ* processing associated with different residence times.


*Keywords:* Mississippi River; DOM; Biomarker; Lignin; Gulf of Mexico

## 1. Introduction

The overall reactivity of riverine dissolved organic matter (DOM) in the coastal zone is largely dependent on its composition, which is controlled in part by source materials and the extent of *in situ* riverine processing (Thurman, 1985; Volk et al., 1997; Findlay and Sinsabaugh, 1999). Although natural differences that exist across different watersheds are important in determining the composition and export of DOM by rivers (Aitkenhead and McDowell, 2000), anthropogenic effects (e.g., agricultural practices) have also been shown to be important (Jacinthe et al., 2001; Guo and Chorover, 2003; Dalzell et al., 2005). DOM inputs from large river

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systems (e.g., Amazon River, Mississippi River), with expansive watersheds, are likely to reflect a heterogeneous mixture of source inputs that have been integrated over space and time (Richey et al., 1990; Hedges et al., 2000). Unlike large river systems, DOM in streams and small rivers is generally derived from local soil and plant litter inputs (Engelhaupt and Bianchi, 2001; Dalzell et al., 2005), and is typically connected to local rainstorm events in the watershed (Cotrim da Cunha et al., 2001). As stream size increases, riverine DOM is gradually degraded downstream (Hedges et al., 2000) and is expected to become more dependent on *in situ* sources (Vannote et al., 1980). In spite of these apparent differences in the sources and processing of DOM in large and small rivers, no studies to our knowledge, have systematically compared the parallels that exist in the temporal and spatial cycling of DOM in rivers of varying sizes within the same flood plain.

Sources and diagenetic state of riverine DOM are important factors controlling the ultimate fate of this DOM in the coastal ocean. Bulk characterization of riverine DOM in large rivers (e.g. lower Mississippi River) is temporally indistinguishable (Duan et al., 2003) because of its inherent molecular complexity and broad spectrum of heterogeneous sources (Thurman, 1985; Spitzy and Leenheer, 1991). Chemical biomarkers, such as lignin phenols, amino acids, sugars, and fatty acids, offer another approach for identifying sources and diagenetic pathways of DOM (Hedges and Ertel, 1982; Dauwe and Middelburg, 1998; Amon and Benner, 2003). In particular, lignin is a macromolecule that has been widely used to trace and quantify land-derived refractory organic matter in marine (e.g., Hedges and Mann, 1979) and river environments (e.g., Bianchi et al., 2004). Lignin oxidation products (e.g., vanillyl, syringyl, and cinnamyl phenols) can provide information on taxonomic source and diagenetic state of terrestrial organic matter (Hedges et al., 1988; Goñi et al., 1993; Opsahl and Benner, 1995). However, recent studies have shown that lignin composition is also controlled by hydrologic and soil mineral sorption processes in drainage basin (Hedges et al., 2000; Kaiser et al., 2001, 2004; Dalzell et al., 2005; Houel et al., 2006).

The purpose of this study was to compare differences in the sources and hydrologic controls on DOM in the lower regions of a large turbid (Mississippi River, USA) and small blackwater river (Pearl River, USA), by comparing seasonal changes in the abundance and composition of lignin phenols. This is a companion paper to Duan et al. (in press), which utilized bulk carbon measurements to characterize temporal changes in DOM within these rivers. While these rivers differ in the size of their watersheds, particle loading, and anthropogenic alterations (e.g., levees, nutrient loading, and damming), both discharge into the coastal zone within close proximity in the north-central Gulf of Mexico. Recent work has suggested, through a conceptual framework, that we need a better understanding of the effects of land-use patterns to broaden our knowledge of the role of streams and rivers in the global carbon cycle (Mayorga et al., 2005). To our knowledge, this is the first study that utilizes biomarkers to better understand the differences in DOM processing in large and small river systems that ultimately deliver DOM to the coastal zone from the same large continental flood plain.

## 2. Materials and methods

### 2.1. Drainage basins

The Mississippi River is one of the largest anthropogenically-impacted rivers in the world, which drains 40% of the continental United States and parts of Canada. On average, the Mississippi River discharges $3.5 \times 10^9$ kg DOC each year to the Gulf of Mexico (Leenheer, 1982; Bianchi et al., 2004). The basin contains one of the most productive farming regions in the world, with cropland representing approximately 58% of the basin (Goolsby et al., 2000). Construction of dams in the primary tributaries has substantially reduced sediment discharge to the Mississippi River by trapping sediment (Keown et al., 1986; Meade et al., 1990). The lower Mississippi River, from Cairo, Illinois to the Gulf of Mexico, is constrained by a system of flood-control levees.

In contrast to the Mississippi River, the Pearl River is a small blackwater river (3rd stream order) draining east-central and southwest Mississippi and southeastern Louisiana; it enters into the Gulf of Mexico via Lake Borgne and the Mississippi Sound. The Pearl River is approximately 790 km long and drains an area of 22,690 $km^2$. The drainage basin is dominated by natural forest (43%), which includes evergreen, deciduous and mixed-forests, followed by agricultural regions (27%). Marshy and/or swampy areas make up 10% of the land cover and are distributed mainly along the river corridor (Pearl River Team, 2000).

### 2.2. Sample collection and processing

Monthly water samples were collected from September 2001 to August 2003 in the lower Mississippi River and from August 2001 to July 2003 in the Pearl River. Sampling sites in the lower Mississippi and Pearl Rivers were located upstream of the U.S. Hwy 190 Bridge, north of Baton Rouge, Louisiana and near Stennis Space Center (NASA), Mississippi, respectively (Fig. 1).

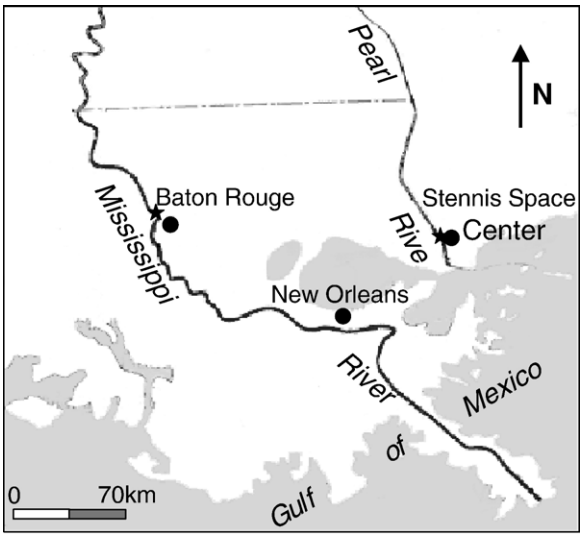


Fig. 1. Map of the lower Mississippi (MR) and the Pearl Rivers (PR). Water samples were collected from the Mississippi River above Baton Rouge (LA), and from the Pearl River near Stennis Space Center (MS) (stars in the map).

Whole water samples were collected midstream in 2 L brown acid-washed polycarbonate bottles (in duplicate, just below the surface) in both rivers for the determination of total organic carbon concentration (TOC), UV absorbance and chlorophyll-*a* (chl-*a*) concentration. Approximately 40 L of filtered water were also collected midstream by pumping (Masterflex pump) water through a 0.2-μm Nuclepore filter cartridge (Whatman Co., England) for collection of high molecular weight (HMW) DOM. All collected water samples were put on ice in a cooler and transported to Tulane University within 1 to 2 h. A known volume of each whole water sample (80 to 150 mL) was filtered through pre-weighed Whatman GF/F filters (25 mm diameter). Filtrates and filters were kept frozen at −80 °C until analyses. HMW DOM was collected from pre-filtered water samples using an Amicon Proflux Tangential System Model $M_{12}$ and a single spiral-wound ultrafiltration cartridge with nominal pore size 1 kDa (Separation Engineering Inc., CA). A carbon mass balance was calculated for each HMW DOM sample. Percent recovery of total DOC during the ultrafiltration process ranged from 91.0% to 110.7%, indicating minimal loss and/or contamination for the mass balance of bulk carbon. The ultrafiltration cartridge was checked for integrity according to methods described by Guo and Santschi (1996). Immediately after ultrafiltration, HMW DOM was frozen, freeze-dried with a LABCONCO (Freezone-6) System, and stored (dry) in a $N_2$ atmosphere. Water discharge data for the Mississippi River (at Tarbert Landing, LA) and the Pearl River (at Bogalusa, LA) were kindly provided by the U.S. Army Corps of Engineers and U.S. Geological Survey, respectively.

### 2.3. Analytical procedures

After 100 μL of 2 N HCl was added to remove inorganic carbon, HMW DOM or filtered water samples were measured for total organic carbon on a Shimazu TOC-$V_{CSH/CSN}$, by using high-temperature catalytic oxidation (HTCO) (Guo et al., 1994). Ultraviolet absorbance at the specific wavelength of 254 nm of filtered water samples, a general indicator of the character and aromaticity of chromophoric dissolved organic matter (CDOM) (Chin et al., 1994), were collected using a 1601 UV/VIS spectrophotometer (Shimadzu Corp., Japan). Chl-*a* was extracted by sonication using 100% HPLC-grade acetone and analyzed by high performance liquid chromatography (HPLC) (Waters, MA) coupled with an on-line 996 photodiode array detector (PDA) and fluorescence detector (Shimadzu-RF 535) as described by Bianchi et al. (1995) and Chen et al. (2001).

Freeze-dried HMW DOM samples collected from the lower Mississippi and Pearl Rivers were analyzed for lignin phenols using the cupric oxide method described by Hedges and Ertel (1982), and modified by Goñi and Hedges (1992). Lyophilized HMW DOM samples were weighed to include 3 to 5 mg of organic carbon and transferred to stainless steel reaction vessels. Samples were digested with CuO in 2 N NaOH and in the absence of $O_2$ at 150 °C for 3 h. Reaction products were extracted with diethyl ether, dried, and converted to trimethylsilyl derivatives with trimethylsilane (TMS) using bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) as a derivatizing agent. Lignin oxidation products were analyzed with a Varian model CP 3800/2000 gas chromatograph/mass spectrometric detector (GC–MS). Quantification was based upon an internal standard (ethyl vanillin) and new response factors where generated with each batch by using a mixed standard of the target compounds. The average standard deviations, based upon two replicates ($n=2$), for the sum of lignin phenols is less than 8% while that for individual compounds ranged from 1% to 19%. Eight lignin phenols (vanillin, acetovanillone, syringaldehyde, vanillic acid, acetosyringone, syringic acid, *p*-coumaric acid and ferulic acid) were quantified and used as molecular indicators for source and diagenetic state of vascular plant tissue. Lambda-6 ($\Lambda_6$) is defined as the sum of vanillyl (vanillin, acetovanillone, vanillic acid) and syringyl (syringaldehyde, acetosyringone, syringic acid) phenols, while Lambda-8 ($\Lambda_8$) also includes the cinnamyl (*p*-coumaric and ferulic acid) phenols. The ratios of total amount of cinnamyl and syringyl phenols to vanillyl

phenols represent as C/V and S/V, and ratios of vanillic acid to vanillin and syringic acid to syringaldehyde were abbreviated as Ad/Al)v and (Ad/Al)s, respectively.

### 2.4. Statistical analyses

Correlation analysis was performed using Spearman's rank correlation coefficient (EXCEL 97). Statistically significant differences between the two rivers were determined using a one-way ANOVA (two-tailed, $\alpha = 0.01$) in SPSS. Means are reported with a 95% confidence interval.

## 3. Results

### 3.1. Total dissolved organic carbon, UV absorbance and chl-a

Water discharge from the lower Mississippi River was characterized by large seasonal shifts that were

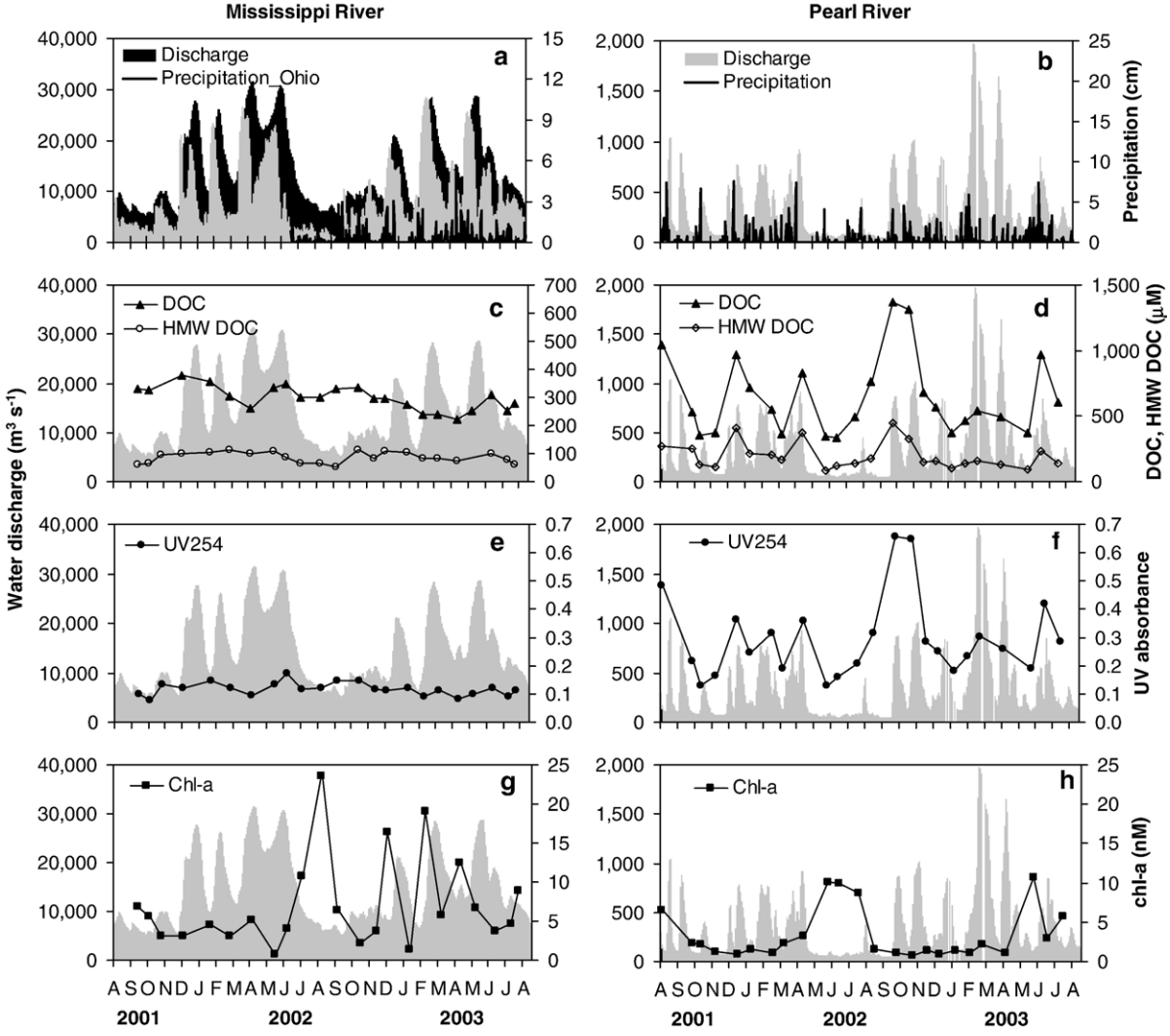


Fig. 2. Water discharge, precipitation, DOC, HMW DOC, ultraviolet (UV) absorbance in 254 nm and chlorophyll-*a* (chl-*a*) concentrations, in the Mississippi River (a, c, e, g) at Baton Rouge and in the Pearl River (b, d, f, h) at Stennis Space Center from August 2001 to August 2003. Data of water discharge and precipitation were obtained from U.S. Geological Survey and U.S. Army Crops of Engineers. (a) Area graphs from back to front are water discharges for the lower Mississippi River from Tarbert Landing and the Ohio River from Metropolis (IL); data of precipitation are means of seven hydrological stations in the mainstem of the Ohio River, and the data are not available before July 2002. (b) Water discharge and precipitation were obtained from Bogalusa (LA) and Columbia (MS), respectively.

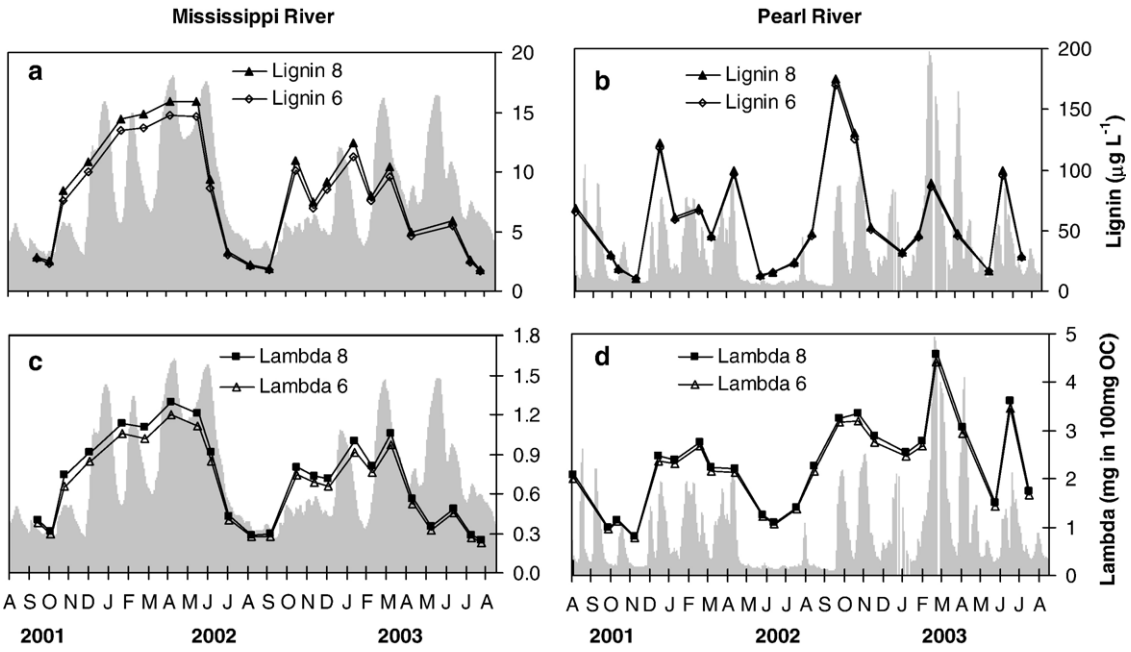


Fig. 3. Seasonal variations in the total lignin phenol concentrations and yields ($\Lambda_6$ and $\Lambda_8$) in HMW DOM collected from the lower Mississippi (a, c) and Pearl Rivers (b, d). The area graphs in the background are for water discharge (same below).

coupled with changes in the Ohio River – the major contributor of water to the Mississippi River (Fig. 2a). In contrast, water discharge for the Pearl River, measured at Bogalusa, LA, was an order of magnitude lower and characterized by a high frequency temporal variability (Fig. 2b). Water discharge in the Pearl River was coupled with local rainstorm events – with peaks in precipitation preceding water discharge.

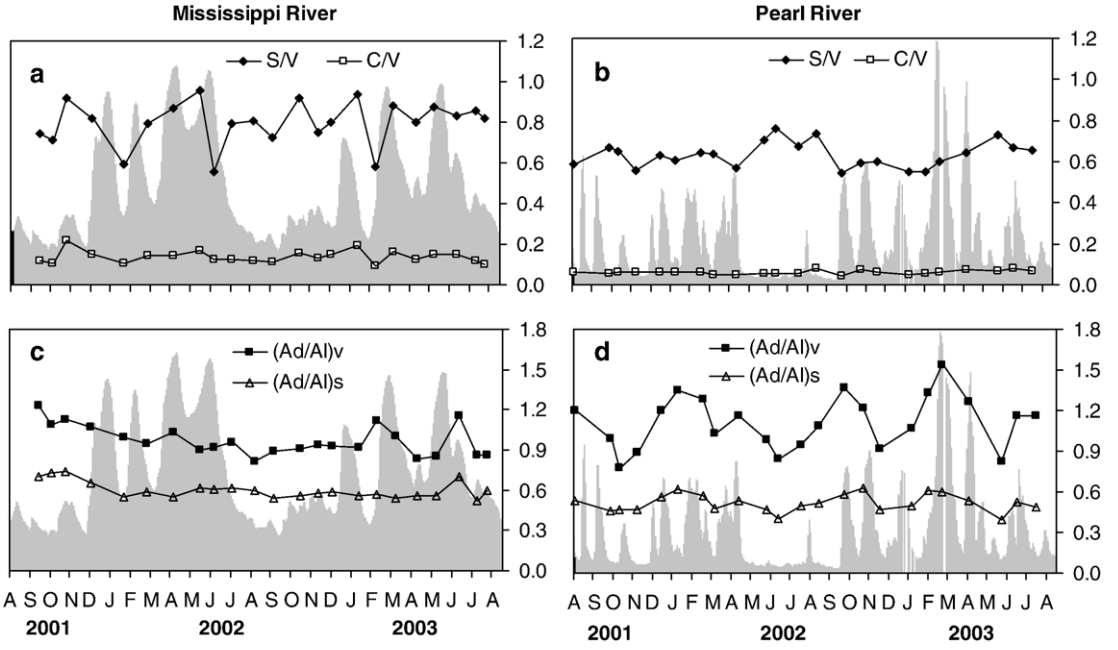


Fig. 4. Seasonal variations in the composition of total lignin phenol in HMW DOM collected from the lower Mississippi (a, c) and Pearl Rivers (b, d). C/V: ratios of cinnamyl/vanillyl phenols; S/V: ratio of syringyl/vanillyl phenols.

Table 1
Lignin phenol yields from HMW DOM collected in the lower Mississippi and Pearl Rivers

| River/Date | $Q$ | $\Lambda_8$ | VAL | VON | VAD | SAL | SON | SAD | FAD | CAD |
|---|---|---|---|---|---|---|---|---|---|---|
| MR 9/14/01 | 6412 | 0.82 | 0.07 | 0.06 | 0.09 | 0.07 | 0.05 | 0.05 | 0.01 | 0.01 |
| MR 10/5/01 | 5800 | 0.68 | 0.06 | 0.04 | 0.07 | 0.05 | 0.04 | 0.04 | 0.01 | 0.01 |
| MR 10/26/01 | 9968 | 0.73 | 0.13 | 0.07 | 0.14 | 0.13 | 0.08 | 0.10 | 0.04 | 0.03 |
| MR 12/5/01 | 14224 | 0.93 | 0.18 | 0.09 | 0.19 | 0.18 | 0.08 | 0.12 | 0.04 | 0.03 |
| MR 1/23/02 | 9828 | 1.24 | 0.27 | 0.12 | 0.27 | 0.20 | 0.08 | 0.11 | 0.04 | 0.03 |
| MR 3/1/02 | 13524 | 1.10 | 0.24 | 0.11 | 0.23 | 0.23 | 0.09 | 0.13 | 0.05 | 0.03 |
| MR 4/10/02 | 30700 | 1.29 | 0.25 | 0.13 | 0.26 | 0.28 | 0.12 | 0.16 | 0.05 | 0.04 |
| MR 5/22/02 | 25032 | 1.21 | 0.23 | 0.13 | 0.21 | 0.25 | 0.15 | 0.15 | 0.06 | 0.04 |
| MR 6/12/02 | 27160 | 0.92 | 0.24 | 0.08 | 0.23 | 0.16 | 0.04 | 0.10 | 0.03 | 0.04 |
| MR 7/10/02 | 10248 | 0.42 | 0.10 | 0.04 | 0.09 | 0.09 | 0.04 | 0.05 | 0.01 | 0.01 |
| MR 8/14/02 | 6188 | 0.29 | 0.07 | 0.03 | 0.05 | 0.06 | 0.03 | 0.03 | 0.01 | 0.01 |
| MR 9/12/02 | 6344 | 0.29 | 0.07 | 0.02 | 0.06 | 0.06 | 0.02 | 0.03 | 0.01 | 0.01 |
| MR 10/24/02 | 9431 | 0.80 | 0.16 | 0.08 | 0.14 | 0.17 | 0.09 | 0.10 | 0.03 | 0.03 |
| MR 11/21/02 | 10535 | 0.74 | 0.17 | 0.06 | 0.16 | 0.15 | 0.06 | 0.09 | 0.03 | 0.02 |
| MR 12/12/02 | 8241 | 0.71 | 0.17 | 0.05 | 0.15 | 0.16 | 0.04 | 0.09 | 0.03 | 0.02 |
| MR 1/22/03 | 16171 | 1.00 | 0.21 | 0.08 | 0.19 | 0.23 | 0.09 | 0.13 | 0.05 | 0.04 |
| MR 2/19/03 | 11016 | 0.81 | 0.20 | 0.06 | 0.22 | 0.15 | 0.04 | 0.09 | 0.03 | 0.02 |
| MR 3/19/03 | 22968 | 1.06 | 0.22 | 0.07 | 0.22 | 0.25 | 0.07 | 0.14 | 0.04 | 0.04 |
| MR 4/23/03 | 15066 | 0.56 | 0.13 | 0.06 | 0.11 | 0.12 | 0.05 | 0.06 | 0.02 | 0.02 |
| MR 5/21/03 | 24525 | 0.35 | 0.08 | 0.02 | 0.07 | 0.08 | 0.03 | 0.04 | 0.01 | 0.01 |
| MR 6/25/03 | 18748 | 0.49 | 0.09 | 0.05 | 0.11 | 0.09 | 0.05 | 0.07 | 0.02 | 0.02 |
| MR 7/24/03 | 13197 | 0.28 | 0.05 | 0.02 | 0.04 | 0.05 | 0.02 | 0.02 | 0.01 | 0.01 |
| MR 8/7/03 | 11526 | 0.24 | 0.04 | 0.02 | 0.04 | 0.04 | 0.02 | 0.02 | 0.01 | 0.00 |
| Mean | 14211 | 0.74 | 0.15 | 0.06 | 0.15 | 0.14 | 0.06 | 0.08 | 0.03 | 0.02 |
| PR 8/3/01 | 171 | 2.09 | 0.46 | 0.25 | 0.55 | 0.39 | 0.15 | 0.21 | 0.04 | 0.03 |
| PR 9/28/01 | 99 | 1.00 | 0.23 | 0.12 | 0.23 | 0.21 | 0.08 | 0.10 | 0.01 | 0.02 |
| PR 10/12/01 | 129 | 1.15 | 0.30 | 0.14 | 0.24 | 0.24 | 0.09 | 0.11 | 0.02 | 0.02 |
| PR 11/9/01 | 71 | 0.82 | 0.21 | 0.12 | 0.18 | 0.15 | 0.06 | 0.07 | 0.01 | 0.02 |
| PR 12/17/01 | 575 | 2.46 | 0.53 | 0.28 | 0.64 | 0.47 | 0.18 | 0.27 | 0.04 | 0.04 |
| PR 1/11/02 | 212 | 2.41 | 0.49 | 0.29 | 0.66 | 0.42 | 0.20 | 0.26 | 0.05 | 0.04 |
| PR 2/20/02 | 250 | 2.77 | 0.56 | 0.34 | 0.72 | 0.53 | 0.22 | 0.30 | 0.06 | 0.04 |
| PR 3/11/02 | 128 | 2.23 | 0.51 | 0.28 | 0.53 | 0.46 | 0.17 | 0.22 | 0.03 | 0.03 |
| PR 4/17/02 | 660 | 2.21 | 0.50 | 0.29 | 0.58 | 0.40 | 0.17 | 0.21 | 0.04 | 0.03 |
| PR 5/31/02 | 80 | 1.26 | 0.28 | 0.15 | 0.28 | 0.27 | 0.11 | 0.13 | 0.02 | 0.02 |
| PR 6/19/02 | 52 | 1.10 | 0.26 | 0.13 | 0.22 | 0.26 | 0.10 | 0.10 | 0.02 | 0.02 |
| PR 7/24/02 | 71 | 1.41 | 0.32 | 0.18 | 0.31 | 0.29 | 0.11 | 0.15 | 0.03 | 0.02 |
| PR 8/22/02 | 87 | 1.88 | 0.39 | 0.21 | 0.43 | 0.39 | 0.16 | 0.20 | 0.04 | 0.04 |
| PR 10/1/02 | 739 | 2.71 | 0.58 | 0.34 | 0.79 | 0.46 | 0.21 | 0.27 | 0.04 | 0.03 |
| PR 10/31/02 | 586 | 2.40 | 0.60 | 0.35 | 0.73 | 0.49 | 0.20 | 0.31 | 0.07 | 0.05 |
| PR 11/26/02 | 192 | 2.40 | 0.61 | 0.27 | 0.56 | 0.47 | 0.18 | 0.22 | 0.05 | 0.04 |
| PR 12/18/02 | 297 | 2.21 | 0.55 | 0.26 | 0.55 | 0.41 | 0.16 | 0.20 | 0.04 | 0.03 |
| PR 1/16/03 | 207 | 2.12 | 0.51 | 0.26 | 0.55 | 0.38 | 0.15 | 0.19 | 0.04 | 0.03 |
| PR 2/11/03 | 462 | 2.31 | 0.49 | 0.29 | 0.65 | 0.39 | 0.17 | 0.23 | 0.05 | 0.03 |
| PR 3/5/03 | 1498 | 3.83 | 0.72 | 0.48 | 1.10 | 0.68 | 0.28 | 0.41 | 0.09 | 0.06 |
| PR 4/16/03 | 1306 | 2.56 | 0.52 | 0.31 | 0.66 | 0.50 | 0.19 | 0.27 | 0.06 | 0.05 |
| PR 6/6/03 | 104 | 1.25 | 0.31 | 0.13 | 0.26 | 0.30 | 0.09 | 0.12 | 0.03 | 0.02 |
| PR 6/30/03 | 183 | 3.02 | 0.65 | 0.31 | 0.76 | 0.61 | 0.22 | 0.32 | 0.08 | 0.06 |
| PR 7/30/03 | 115 | 1.44 | 0.30 | 0.18 | 0.35 | 0.29 | 0.12 | 0.14 | 0.03 | 0.03 |
| Mean | 345 | 2.04 | 0.45 | 0.25 | 0.52 | 0.39 | 0.16 | 0.21 | 0.04 | 0.03 |

Abbreviations: $Q$, water discharge ($m^3\ s^{-1}$); $\Lambda_8$ = sum of vanillyl, syringyl and cinnamyl (FAD and CAD) phenols produced from the oxidation of 100 mg of organic carbon (Hedges and Mann, 1979); VAL, vanillin; VON, acetovanillone; VAD, vanillic acid; SAL, syringaldehyde; SON, acetosyringone; SAD, syringic acid; FAD, ferulic acid; CAD, *p*-coumaric acid.
Lignin phenols' yields are all in the units of mg $(100\ mg\ OC)^{-1}$.

Concentrations of DOC, HMW DOC and UV absorbance at 254 nm ($UV_{254}$) in the lower Mississippi River (223–380 μM, 45.3–143 μM, 0.07–0.17) were significantly lower ($p<0.01$, one-way ANOVA, two-tailed) than in the Pearl River (336–1370 μM, 88.5–448 μM, 0.12–0.65). Temporal variations in DOC, HMW DOC, and $UV_{254}$ were minimal in the lower Mississippi River and were not coupled with water discharge (Fig. 2c, e). Conversely, larger seasonal variations in DOC, HMW DOC, and $UV_{254}$ were observed in the Pearl River, and they were all positively correlated with water discharge ($r^2=0.49$, 0.67 and 0.50, $n=22$, $p<0.01$) (Fig. 2d, f). A greater fraction of total DOC (23–47%, $\bar{x}=35\%$) was represented by HMW DOC in the Pearl River than in the lower Mississippi River (13–38%, $\bar{x}=25\%$) ($p<0.01$, one-way ANOVA, two-tailed). The fraction of HMW DOC in the lower Mississippi River was also close to those in other studies in the same regions (Hernes and Benner, 2003; Bianchi et al., 2004). Chlorophyll-*a* concentrations in the lower Mississippi River (0.77–23.6 nM) were about twice as high as in the Pearl River (0.76–10.7 nM), with the highest values (in both rivers) occurring in the summer low-discharge period – followed by additional peaks in winter and spring (in the Mississippi River) (Fig. 2g, h).

### 3.2. Lignin phenols in HMW DOM

Total concentrations of lignin (sum of eight lignin phenols) in HMW DOM from the lower Mississippi River at Baton Rouge ranged from 1.9 to 15.9 μg $L^{-1}$ with a mean of 8.1 μg $L^{-1}$ (Fig. 3a) – similar to prior measurements in the river near Head of Passes (Opsahl and Benner, 1998; Hernes and Benner, 2003). $\Lambda_8$ (0.24 to 1.29 mg (100 mg OC)$^{-1}$), and the ratios of S/V (0.55 to 0.95) and C/V (0.10 to 0.22) and (Ad/Al)v (0.82 to 1.23) (Figs. 3c and 4a, c) were also comparable to those of HMW DOM, collected below New Orleans (Bianchi et al., 2004) and further downstream near Head of Passes (Benner and Opsahl, 2001). Vanillyl was the main component of lignin phenols, followed by syringyl; small differences between $\Lambda_6$ and $\Lambda_8$ were consistent with relatively low amounts cinnamyl in the Mississippi River (Table 1; Fig. 3c). Seasonal variations in lignin concentrations and $\Lambda_8$ values in the lower Mississippi River positively correlated with water discharge during the first year of sampling ($r^2=0.60$, $n=11$, $p<0.01$) but not in the second year (Fig. 3a, c). Ratios of S/V, C/V, (Ad/Al)v and (Ad/Al)s did not correlated with water discharge (Fig. 4a, c).

Compared to the lower Mississippi River, lignin concentrations, $\Lambda_8$ values, and (Ad/Al)v ratios in HMW DOM from the Pearl River were significantly higher ($p<0.01$, one-way ANOVA, two-tailed) (10.7 to 175 μg $L^{-1}$, 0.74 to 4.6 mg (100 mg OC)$^{-1}$, 0.78 to 1.54, respectively), while the ratios of S/V (0.54 to 0.76) and C/V (0.04 to 0.08) were significantly lower ($p<0.01$, one-way ANOVA, two-tailed) (Table 1; Figs. 3 and 4). Lignin concentrations in the Pearl River varied over an order of magnitude seasonally, with the highest values observed during hurricanes (September and October 2002) and the lowest values observed in dry seasons (Fig. 3b). Seasonal variations in $\Lambda_8$ values and (Ad/Al)v positively correlated with water discharge ($r^2=0.71$ and 0.42, $p<0.01$), and S/V was negatively correlated with water discharge ($r^2=0.43$, $p<0.01$), while C/V ratios only showed minimal seasonal changes (Figs. 3d and 4b, d).

## 4. Discussion

### 4.1. Source inputs of terrestrially-derived HMW DOM

#### 4.1.1. Pearl River

High lignin concentrations and $\Lambda_8$ values in Pearl River HMW DOM were likely attributed to inputs of plant litter leachate and soil organic matter from forests and marshes in the drainage basin. A significantly positive relationship between lignin concentrations and water discharge in the Pearl River (Figs. 3b and 6a) indicated non-point source inputs of HMW DOM lignin, which were transported to the river by sporadic rainstorm events. High $\Lambda_8$ values in the Pearl River HMW were consistent with high UV absorbance at 254 nm and the overall terrestrially-derived signature of HMW DOM found using bulk carbon measurements, such as $^{13}C$ NMR (e.g., highly aromatic) (Duan et al., 2003). The increase in $\Lambda_8$ with water discharge (Fig. 6b) and a correlation between $\Lambda_8$ and (Ad/Al)v [and also (Ad/Al)s] (Fig. 6c) further suggested that these non-point sources were rich in lignin and acidic components – most likely terrigenous humic substances from marshes as well as forest soils. Wetlands in river corridors have also been shown to be the major source of terrestrial inputs to Amazon River DOM (McClain et al., 1997). The mean value of $\Lambda_8$ (or $\Lambda_6$) in the Pearl River HMW DOM was close to the other small streams draining wetlands in the Mississippi Deltaic region (Engelhaupt and Bianchi, 2001) and in southeastern USA (Opsahl, 2005). In fact, inputs and mobilization of DOM derived from watershed wetlands and soils have been reported in other studies (see Meybeck, 1982; Alberts et al., 1992; Dalzell et al., 2005). As will be discussed in the next section, local hydrologic inputs from flooded forests and wetland soils,

represent an enriched source of HMW DOM in the lower Pearl River drainage basin.

C/V and S/V ratios in the Pearl River HMW DOM lignin were reflective of inputs from dominant vegetation types (e.g., mixture of woody angiosperms and gymnosperms) and soils in the watershed. Although there were no significant differences in cinnamyl concentrations between the two rivers (Table 1, one-way ANOVA, $p > 0.05$, two-tailed), we did observe significant lower C/V and S/V ratios in Pearl River HMW DOM relative to Mississippi River HMW DOM (Fig. 5). The lower C/V ratios in Pearl River HMW DOM were in agreement with the dominant sources of vascular plants in the Pearl River drainage basin – forests (47%) and marshes (10%) (Pearl River Basin Team, 2000). However, as shown in recent studies (e.g. Hedges et al., 2000; Engelhaupt and Bianchi, 2001; Houel et al., 2006), C/V and S/V ratios in HMW DOM may not always provide accurate indices for source materials of HMW DOM, because of lignin transformations due to selective dissolution/leaching and sorption on minerals in soils. In particular, low C/V ratios of HMW DOM might be the result of selective sorption of cinnamyl phenols on minerals in deep soil horizons (Houel et al., 2006). Thus, the C/V and S/V ratios observed in Pearl River HMW DOM likely reflected both inputs from the dominant woody vegetation in the watershed, in addition to soil mineral effects.

#### 4.1.2. Lower Mississippi River

The relatively wider spread of C/V and S/V ratios of lignin of Mississippi River HMW DOM suggested that HMW DOM in lower Mississippi River were derived from a broader spectrum of sources and soil processes than the Pearl River. This was clearly expected because the larger Mississippi River drainage basin encompasses diverse vegetation, decay processes in soils, climatic events, and anthropogenic effects (Onstad et al., 2000). Other work has shown that $C_4$ plant materials (high C/V ratio [0.25] and enriched $\delta^{13}C$) are the dominant sources of POC in the Missouri River, which drains natural grasslands into the Mississippi River (Onstad et al., 2000; Goñi et al., 1997). Conversely, the other major tributary of the Mississippi River, the Ohio River, has a POC signal that is largely derived from $C_3$ plant materials (low C/V ratio [0.07] and depleted $\delta^{13}C$) (Onstad et al., 2000; Goñi et al., 1997). The range of C/V ratios in HMW DOM from lower Mississippi River in this study and another study (0.10–0.22) (e.g. Bianchi et al., 2004) were within the range of C/V ratios found in POC of these two tributaries – suggestive of linkages between POC and HMW DOM lignin sources. C/V ratios of HMW DOM and POM in the Amazon River were also found to be similar (Hedges et al., 2000). While we do see some possible linkages here between lignin sources in POM and HMW DOM, other work has shown a de-coupling of $C_4$ particulate materials and HMW DOM in the lower Mississippi River (Bianchi et al., 2004). Using compound-specific isotope analyses (CSIA) of lignin, Bianchi et al. (2004) attributed this de-coupling to differences in organic matter distribution among particle size classes. More specifically, it was suggested that $C_4$ lignin in POM was not being converted (via microbial decay) to HMW DOM as readily as $C_3$ lignin because of the association of $C_4$ organic matter with finer sediments. These molecular and bulk signatures of terrestrially-derived sources in POM and HMW DOM further support the importance of temporal changes in the selective partitioning of lignin within the drainage basin – which are strongly controlled by hydrologic conditions.

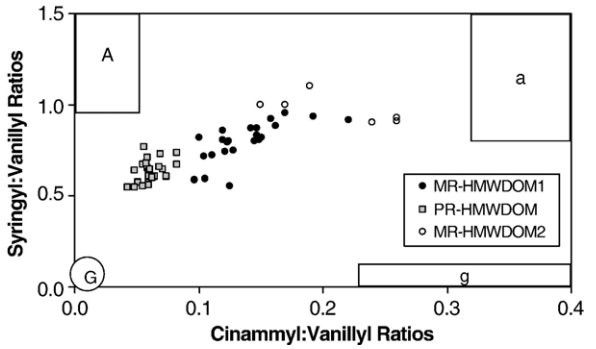


Fig. 5. Plot of cinnamyl/vanillyl (C/V) vs. syringyl/vanillyl (S/V) phenol ratios for HMW DOM collected from lower Mississippi and Pearl Rivers (HMW MR1 and HMW PR). Included are the compositional ranges (delineated by dotted lines) of major vascular plant tissues (Hedges et al., 1988). Tissue abbreviations: G, gymnosperm woods; g, gymnosperm needles; A, angiosperm woods; a, angiosperm leaves and grasses. HMW MR2 stands for data published by Bianchi et al. (2004).

The lower lignin concentrations in the Mississippi River HMW DOM are in part, due to a lower export rate of lignin from agricultural soils (see next section), a dilution effect from phytoplankton-derived DOM, and possible photochemical effects. Chl-*a* concentrations in the lower Mississippi River were significantly higher than in the Pearl River (Fig. 2e, f). In fact, recent work has shown that chl-*a* concentrations in the lower river at certain times in the year, rival what is found in the highly productive Mississippi River plume (Duan and Bianchi, 2006). These high chl-*a* concentrations in the Mississippi River are due to rising nutrient concentrations accompanied by a reduction in total suspended solids. Moreover, it was recently shown that this relatively high

abundance of phytoplankton biomass does in fact contribute to the HMW DOM pool (via grazing, microbial decay, and/or cell lysis) in the lower Mississippi River (Bianchi et al., 2004).

Other possible explanations for the lower lignin concentrations in the Mississippi River HMW DOM, which we only provide speculation on here, are photochemical and microbial oxidation of lignin during its downriver transport, as it periodically passes through surface waters. Past photochemical work in the lower Mississippi River showed significant losses of dissolved lignin in just over 28 days of exposure to sunlight (Opsahl and Benner, 1998). However, photochemical oxidation will not be as significant in the lower river as in the river plume, because high loading of suspended particles in the river greatly reduces the availability of light in the water column. In fact, a recent spatial survey showed only minor losses of total DOC and specific ultraviolet absorbance (SUVA) in the lower reach of the Mississippi River (Dagg et al., 2005). Photochemical oxidation of lignin is more likely to occur in the upper river, where suspended particulate matter concentration (SPM) is low and the river is shallower – in addition to presence of reservoirs and navigation pools which are characterized by low SPM and long hydraulic residence times (Wiener et al., 1996; Wehr and Thorp, 1997). The potential for the microbial oxidation of lignin by bacteria that are capable of decomposing lignin, may provide another mechanism for the losses of lignin in the Mississippi River HMW DOM. Further work are clearly needed in the upper watershed of the Mississippi River to determine if photochemical and microbial processes have any significant effects on lignin concentrations in the lower Mississippi River.

### 4.2. Hydrologic controls on inputs of terrestrially-derived HMW DOM

Seasonal changes in the composition and abundance of terrestrially-derived HMW DOM in the Pearl River are controlled by local hydrologic processes in this small watershed. As discussed earlier, the concentration and composition of lignin in soil leachates can be the result of a variety of processes (e.g., selective dissolution/leaching followed by sorption on minerals) in soil horizons. For example, selective oxidation of lignin moieties from fresh plant litter on the forest floor often releases highly altered aromatic constituents that can be incorporated into soil solutions as HMW fractions (Kaiser and Guggenberger, 2000; Kaiser et al., 2001). Significantly higher C/V and (Ad/Ad)v signatures of soil organic matter have been observed in deep mineral layers compared to surface horizons of less-disturbed soils (Houel et al., 2006). This suggests transport of these fractions from surface plant litter layers and selective strong sorption on clay minerals in deep horizons (Kaiser and Guggenberger, 2000; Kaiser et al., 2001, 2004; Rumpel et al., 2002). The interaction of these processes with local rainstorm flushing events is likely to have had significant effects on the export of lignin from the watershed to the Pearl River.

Large seasonal changes in lignin concentration and composition in the Pearl River HMW DOM were likely in response to local rainfall/flooding events. Flushing of vascular plant inputs from watershed soils during flooding events has been shown to be an important source of DOM to aquatic systems (Guggenberger and Zech, 1993). During extended dry seasons (e.g. May to July 2002 in this study), when base-flow dominates, river water has been shown to be largely derived from groundwaters in deep soil layers (Fetter, 1990), which are typically low in $\Lambda_8$ and (Ad/Al)v ratios (Kaiser et al., 2004). Thus, during the dry seasons, when terrestrial OM inputs from soils are relatively small, the impact of any dilution effects from *in situ* derived DOC (e.g., phytoplankton sources) would likely be higher (high chl-*a*, see Fig. 2), especially since there is more light availability during this time. Conversely, during sporadic rainstorm events or high-water discharge periods (e.g. September 2002), overland flow and interflow likely dominated, allowing for greater inputs of DOM from surface plant litter and topsoils high in ($\Lambda_8$) and (Ad/Al)v ratios (Kaiser et al., 2004). Other work has shown that lignin content and composition in soil inputs also matched forest floor leachates during rainstorm events (Kaiser and Guggenberger, 2005).

HMW DOM from the lower Mississippi River represented a larger integrated signal of terrestrially-derived OM from the upper watershed soils, as indicated by seasonal variation in lignin phenol concentration that were coupled with river water discharge. Unlike total DOC (Fig. 2), lignin phenol concentrations and $\Lambda_8$ showed large seasonal variations, with higher concentrations during high-discharge and lower concentrations during low-discharge periods (Fig. 3). However, lignin phenol concentrations and $\Lambda_8$ in the lower Mississippi River were not as strongly correlated with water discharge as in the Pearl River (Fig. 6a, b) – with some exceptions in the first year of this study (Fig. 3). The reason may be that DOM in large rivers record an integrated signal from a more expansive watershed, making them more de-coupled to local hydrologic events than in smaller river watersheds. The same

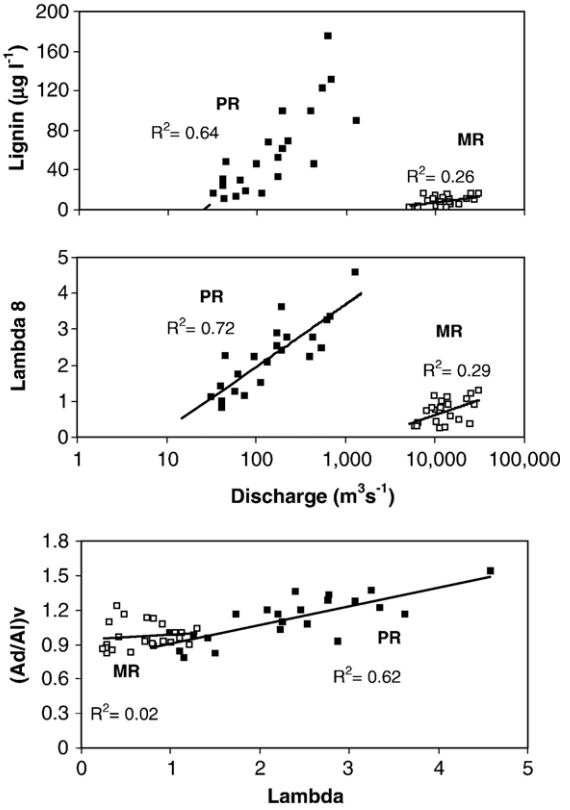


Fig. 6. Plots of concentration of lignin phenols (a) and $\Lambda_8$ (b) vs. water discharge, and (Ad/Al)v ratio vs. $\Lambda_8$ (c) in lower Mississippi and Pearl Rivers.

mechanism may in part explain the lack of seasonality in the ratios of S/V, C/V, (Ad/Al)v and (Ad/Al)s in the lower Mississippi River. The lack of seasonal variation in the composition of lignin phenols in the lower Mississippi River HMW DOM was also observed by Bianchi et al. (2004). As discussed earlier, another explanation for the difference in seasonal changes in lignin concentration and total DOC is a "dilution effect" from algae-derived DOM. Thus, we propose that lignin phenols in the lower Mississippi River HMW DOM were more correlated with high river discharge than was total DOC, because the former was more linked with inputs from soils during flushing events in the upper watershed, while the latter was more controlled by *in situ* contributions from riverine phytoplankton.

### *4.3. Land-use and storage effects on inputs of terrestrially-derived HMW DOM*

Differences in land-use practices and local climatic events within the drainage basins of these rivers appear to be important in controlling the composition and total amount of terrestrially-derived inputs to riverine HMW DOM. For example, significantly lower $\Lambda_8$ values and (Ad/Al)v ratios in HMW DOM from the lower Mississippi River (Table 1 and Fig. 6c), compared to the Pearl River, may have resulted from a lower export rate of lignin from agricultural soils due to lower carbon storage. Currently about 58% of the Mississippi drainage basin is cropland, with natural forests accounting for only 18% of the total area (Goolsby et al., 2000). Deforestation has been shown to increase export rate of total DOM and lignin, due to greater microbial activity induced by an increased temperature (Kalbitz et al., 2004) and enhanced soil erosion (Farella et al., 2001), respectively. However, the long-term replacement of forests/grasslands with croplands, seems to have decreased the lignin export rate due to lower carbon storage in agricultural soils. Intensive agricultural activities (e.g. tilling) (Donigian et al., 1994) keep soils well-aerated and open to sunlight and biological attack, thereby enhancing carbon cycling and reducing the accumulation of humic substance and lignin in subsoils (Reicosky et al., 2002). For example, studies on soil organic matter showed that deforestation and progressive cultivation decreased the content of soil humic substances and lignin phenols, and that the resulting humic pool was more depleted in alkyl components and less hydrophobic than in forested conditions (Lobe et al., 2002; Spaccini et al., 2006). The rapid processing of crop organic matter also leads to the changes in composition of DOM exported from agricultural soil. Recent studies showed that cultivation resulted in the production of low molecular weight (LMW) (<1 kDa) compounds (Wagener et al., 1998; Keim and Kögel-Knabner, 2003) and greater transport of LMW DOM through agricultural soils compared to soils in natural ecosystems (Guo and Chorover, 2003; Dalzell et al., 2005). All of these studies clearly illustrate that, with continued changes in global climate and land-use patterns, the cycling of organic carbon at the interface between terrestrial and aquatic systems is very complex and continually changing. Our work provides only a small linkage to such global issues but nevertheless supports that LMW DOM predominates over HMW DOM in the Mississippi River and that land-use patterns in drainage basins clearly have a dramatic effect on the composition of DOM in rivers.

## 5. Conclusions

A comparison of seasonal changes in the abundance and compositions of lignin in HMW DOM from the Pearl River and the Mississippi River revealed that natural and anthropogenic differences in the hydrologic processing of

terrestrial organic matter in these different watersheds can have major effects on the delivery of DOM to the northern Gulf of Mexico. While the terrestrially-derived signature of HMW DOM in both rivers is very similar, the hydrologic controls that determine the partitioning of DOM in soils and *in situ* processing during river transport are likely very different. In the Pearl River, local rainfall events are the primary driving mechanism for HMW DOM export, while upper drainage basin hydrologic processes controls a more integrated and diluted signature of terrestrially-derived HMW DOM in the lower Mississippi River. The overall dilution of terrestrially-derived HMW DOM occurs due to *in situ* processing (dilution from algal inputs) and the lack of fresh inputs (due to the levee system) during transport to the lower Mississippi River. Furthermore, based on this work and other studies in the Mississippi River watershed, the composition of HMW DOM from the lower Mississippi River appears to be largely controlled by anthropogenic (e.g., agricultural) activities.

This comparison between a small blackwater river and large turbid river in adjacent watersheds that empty in close proximity in the northern Gulf of Mexico, reveals the importance of local versus more distant processing of organic matter inputs to the composition and abundance of riverine DOM. If we are to better understand the controls of organic matter delivery to the coastal zone from both small and large rivers, sampling strategies need to be adjusted to account for the different scales in hydrologic response time and also *in situ* processing with different residence time. Clearly, as recent work has shown, anthropogenic processes now dominate over natural processes in controlling biogeochemical processes in river systems around the world, and we are reminded that we are operating in the anthropocene (Meybeck, 2002).

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